EXHIBIT 1

SURFACTANTS AND INTERFACIAL PHENOMENA

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Surfactants and Interfacial Phenomena

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suggested by the existence of persistent foam in cases where the film is known *not* to have great surface viscosity — and this is true of foaming solutions of purified surface-active agents, where it is known that the surface films are not particularly coherent. In these cases, it has been suggested that when the film becomes very thin (<0.2 μm or 200 nm), stability is obtained chiefly because of the electrical repulsion between the ionic double layers associated with the adsorbed ionic surfactant on the two sides of the liquid film. Since the addition of electrolyte to the foaming solution causes compression of the electrical double layers associated with the surface films, such addition decreases their mutual repulsion. This is believed to account for the decreased thickness of liquid films with increase in their electrolyte content (Davies, 1963) and for the decreased stability of many foams on the addition of electrolyte.

III. THE RELATIONSHIP OF SURFACTANT CHEMICAL STRUCTURE TO FOAMING IN AQUEOUS SOLUTION

In foaming as in other surface properties, correlations between surfactant structure and foaming in aqueous solution require a distinction between the efficiency of the surfactant, its bulk phase concentration required to produce a significant amount of foam, and its effectiveness, the maximum foam height obtained with the surfactant solution regardless of its concentration. Distinction must also be made between foam production, measured by the height of the foam initially produced, and foam stability, the height after a given amount of time. Therefore in comparing the foaming properties of different surfactants, the term *foaming ability* must be clearly defined. In addition, such conditions as the method used to produce the foam, the temperature of the solution, the hardness of the water used, and its electrolyte content must all be specified. Since most of the foaming data on surfactants with clearly defined structures have been obtained by use of the Ross-Miles method (Ross, 1953), the structural correlations discussed here are based mainly on data obtained by what method.

In the Ross-Miles method, 200 ml of a solution of surfactant contained in a pipette of specified dimensions with a 2.9 mm I.D. orifice are allowed to fall 90 cm onto 50 ml of the same solution contained in a cylindrical vessel maintained at a given temperature (often 60°C) by means of a water jacket. The height of the foam produced in the cylindrical vessel is read immediately after all the

solution has run out of the pipette ("initial foam height") and then again after a given amount of time (generally, 5 minutes).

A. Efficiency as a Foaming Agent

Foam height generally increases with increase in surfactant concentration below the critical micelle concentration until the neighborhood of the CMC is reached, in which region foam height reaches a maximum. Thus the CMC of a surfactant is a good measure of its efficiency as a foaming agent; the lower the CMC, the more efficient the surfactant as a foamer. Those structural factors that produce a lower critical micelle concentration — for example, increased length of the hydrophobic group — would therefore be expected to increase the efficiency of the surfactant as a foaming agent. The addition of neutral electrolyte (which decreases the CMC of the surfactant) increases the efficiency of ionic surfactants. Table 7-1 lists the bulk phase concentrations at which foam height reaches a maximum for some aqueous solutions of surfactants, together with their CMCs at the same temperature at which the foaming data were obtained. It is apparent that surfactants with longer hydrophobic groups are more efficient, but not necessarily more effective, foaming agents. Since the Ross-Miles foaming test is usually done at 0.25% surfactant concentration, equivalent to about 8×10^{-3} M for most surfactants, only those materials having CMCs greater than that will not have reached their maximum foam volume at that concentration.

B. Effectiveness as a Foaming Agent

The effectiveness of a surfactant as a foaming agent appears to depend on both its effectiveness in reducing the surface tension of the foaming solution and on the magnitude of its intermolecular cohesive forces. The volume of foam produced when a given amount of work is done on an aqueous solution of surfactant to create foam depends on the surface tension of the solution, since the minimum amount of work required to produce the foam is $\gamma \cdot \Delta A$, the product of the surface tension and the change in the area of the liquid/gas interface as a result of the foaming. The lower the surface tension of the aqueous solution, the greater appears to be the volume of foam of the same average bubble size produced by a given amount of work under the same foaming conditions (Rosen, 1969). It has also been

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Table 7–1. Foaming Efficiency of Aqueous Surfactant Solutions (Ross-Miles Method[a])

Surfactant	Temp. (°C)	Concentration (M) to reach maximum foam height	CMC	Height (mm)	Reference
$p\text{-}C_8H_{17}C_6H_4SO_3^-Na^+$	60	13×10^{-3}	16×10^{-3}	165	Gray, 1955
$p\text{-}C_{10}H_{21}C_6H_4SO_3^-Na^+$	60	4.5×10^{-3}	3×10^{-3}	185	Gray, 1965
$o\text{-}C_{12}H_{25}C_6H_4SO_3^-Na^+$	60	4×10^{-3}	3×10^{-3}	205	Gray, 1955
$p\text{-}C_{12}H_{25}C_6H_4SO_3^-Na^+$	60	4×10^{-3}	1.2×10^{-3}	200	Gray, 1955
$o\text{-}C_{11}H_{23}CH(CH_3)C_6H_4SO_3^-Na^+$	60	8×10^{-3}	—	195	Gray, 1965
$p\text{-}C_{11}H_{23}CH(CH_3)C_6H_4SO_3^-Na^+$	60	8×10^{-3}	5×10^{-3}	215	Gray, 1955
$p\text{-}C_7H_{15}CH(C_4H_9)C_6H_4SO_3^-Na^+$	60	7×10^{-3}	4×10^{-3}	230	Gray, 1955
$C_5H_{11}CH(C_5H_{11})SO_4^-Na^+$	60	10×10^{-3}	83×10^{-3}	130	Dreger, 1944
$C_{12}H_{25}SO_3^-Na^+$	60	11×10^{-3}	13×10^{-3}	210	Rosen, 1969
$C_{12}H_{25}SO_4^-Na^+$	46	5×10^{-3}	9×10^{-3}	205	Dreger, 1944
$C_{11}H_{23}CH(CH_3)SO_4^-Na^+$	46	5×10^{-3}	6.5×10^{-3}	205	Dreger, 1944
$C_6H_{13}CH(C_6H_{13})SO_4^-Na^+$	46	$>15 \times 10^{-3}$	19×10^{-3}	220	Dreger, 1944
$C_{14}H_{29}SO_3^-K^+$	60	3×10^{-3}	3×10^{-3}	217	Rosen, 1969
$C_{14}H_{29}SO_4^-Na^+$	46	3×10^{-3}	2.3×10^{-3}	225	Dreger, 1944
$C_{13}H_{27}CH(CH_3)SO_4^-Na^+$	46	3×10^{-3}	1.7×10^{-3}	220	Dreger, 1944
$C_7H_{15}CH(C_7H_{15})SO_4^-Na^+$	46	5×10^{-3}	6.7×10^{-3}	240	Dreger, 1944
$C_{16}H_{33}SO_3^-K^+$	60	0.8×10^{-3}	0.9×10^{-3}	233	Rosen, 1969
$C_{16}H_{33}SO_4^-Na^+$	60	0.8×10^{-3}	0.7×10^{-3}	220	Rosen, 1969
$C_{15}H_{31}CH(CH_3)SO_4^-Na^+$	46	$<1 \times 10^{-3}$	0.5×10^{-3}	212	Dreger, 1944
$C_8H_{17}CH(C_8H_{17})SO_4^-Na^+$	46	4×10^{-3}	2.3×10^{-3}	245	Dreger, 1944
$p\text{-}C_9H_{19}CH(CH_3)C_6H_4SO_3^-Na^+$	60	13×10^{-3}	—	190	Gray, 1965
$p\text{-}C_{13}H_{27}CH(CH_3)C_6H_4SO_3^-Na^+$	60	4×10^{-3}	—	175	Gray, 1965
$p\text{-}C_{15}H_{31}CH(CH_3)C_6H_4SO_3^-Na^+$	60	0.7×10^{-3}	—	126	Gray, 1965

[a] Ross, 1953.

suggested (Dreger, 1944) that the rate of attainment of surface tension reduction may also be a factor in determining the effectiveness of a surfactant as a foaming agent. Therefore branched-chain surfactants and those containing centrally located hydrophobic groups, which are believed to diffuse rapidly to the interface, would be expected to produce higher volumes of initial foam. However, not only must the surfactant produce the foam, it must also maintain it—the foam must have appreciable stability. This should require an interfacial film with sufficient cohesion to impart elasticity and mechanical strength to the liquid lamellae enclosing the gas in the foam. Since interchain cohesion increases with increase in the length of the hydrophobic group, this may account for the observation that foam height often goes through a maximum with increase in the length of the chain. Too short a chain probably produces insufficient cohesiveness, whereas too great a length produces too much rigidity for good film elasticity (or too low a solubility in water).

Since branched-chain surfactants and those with centrally located hydrophilic groups can depress the surface tension of water to lower values than isomeric straight-chain compounds or those with terminally located hydrophilic groups (Chapter 5, Section II), the former types of compounds would be expected to show higher initial foam heights than the latter. However, since hydrophobic groups with branches have weaker intermolecular cohesive forces than straight-chain ones, the former would be expected to show less foam stability. The result of these two opposing factors is that when the hydrophilic group of a straight-chain surfactant is moved from a terminal to a more central position in the molecule, foam heights generally increase, provided that the materials are all compared above their critical micelle concentrations where foaming is at a maximum. This is necessary here because the shift of the hydrophilic group to a more central position in the molecule causes an increase in the CMC of the surfactant with a resulting decrease in its efficiency as a foaming agent. Surfactants with highly branched chains, on the other hand, generally show lower foam heights than isomeric straight-chain materials, except where the length of the hydrophobic group becomes too long for straight-chain compounds to have adequate water solubility for good foaming (e.g., >16 carbon atoms at 40°C). Presumably for a similar reason, 2,5-di-*n*-alkylbenzenesulfonates show lower foam heights and stabilities than the corresponding *p*-*n*-alkylbenzenesulfonates (Kolbel, 1960*b*). Since branched-chain hydrophobic groups show greater water solubility than straight-chain ones and intermolecular cohesive forces increase with increase in chain length, good foaming at 40°C can be obtained with branched-chain surfactants containing up to 20 carbon atoms and foam heights in the C_{20} branched compounds appear to exceed those obtained with any shorter straight-chain compounds (Kölbel, 1960*a*).

In ionic surfactants the effectiveness of foaming appears to depend also on the nature of the counterion, those with smaller counterions showing greater initial foam heights and foam stabilities. Thus in the dodecyl sulfate series, the effectiveness decreases with increased size of the counterion in the order $NH_4^+ > (CH_3)_4N^+ > (C_2H_5)_4N^+ > (C_4H_9)_4N^+$ (Kondo, 1960).

Table 7-2 lists the foaming effectiveness of some surfactants in aqueous solution.

In distilled water at room temperature, sodium alkyl sulfates and soaps with saturated, straight-chain hydrophobic groups containing 12—14 carbon atoms seem to show the best foaming capacities (Broich, 1966); at higher temperatures, homologous materials with somewhat longer chains give optimum foaming. Thus at 60°C, saturated straight-chain alkyl sulfates containing 16 carbon atoms, palmitate soaps, dodecyl- and tetradecylbenzenesulfonates (hydrophobic groups equivalent to 15.5—17.5 carbon chains), and α-sulfoesters containing 16—17 carbon atoms show maximum foaming power (Weil, 1954, 1966; Gray, 1955; Kölbel, 1959; Micich, 1966; Stirton, 1962). Near the boiling point, C_{18} compounds are best. Since interchain cohesion must overcome thermal agitation of the molecules, which increases with increase in temperature, it is to be expected that optimum chain lengths should increase with increase in temperature. The disodium salts of α-sulfocarboxylic acids produce much less foam than the monosodium salts of α-sulfoesters, presumably because increased electrostatic repulsion between hydrophilic groups counters inter-chain cohesive forces.

In hard water somewhat shorter anionic compounds seem to give optimum foaming, probably because of the greater cohesiveness of anionic surface films in the presence of Ca^{++}. Thus in 300 ppm $CaCO_3$ solution at 60°C, C_{12}—C_{14} saturated straight-chain alkyl sulfates show the highest foaming capacities (Weil, 1954).

Nonionic surfactants generally produce less foam and much less stable foam than ionic surfactants in aqueous media. These effects are probably due to the larger surface area per molecule and the absence of highly charged surface films in these foams. In polyoxyethylenated nonionics both foam stability and foam volume reach a maximum at a particular oxyethylene chain length and then decrease (Schick, 1963). This is ascribed to a maximum in

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Table 7—2. Foaming Effectiveness of Aqueous Surfactant Solutions (Ross-Miles Method[a])

Surfactant	Conc. (%)	Temp. (°C)	Foam Height (mm)			Reference
			Distilled Water		300 ppm $CaCO_3$	
			Initial	After Time (min)	Initial	
$C_{12}H_{25}OSO_3^-Na^+$	0.25	60	220	175(5)	240[b]	Weil, 1966, 1954
$C_{12}H_{25}SO_3^-Na^+$	0.25	60	—	205(1)	—	Rosen, 1969
$C_{14}H_{29}OSO_3^-Na^+$	0.25	60	231	184(5)	246[b]	Weil, 1954
$C_{14}H_{29}SO_3^-Na^+$	0.11	60	—	214(1)	—	Rosen, 1969
$C_{16}H_{33}OSO_3^-Na^+$	0.25	60	245	240(5)	178[b]	Weil, 1966, 1954
$C_{16}H_{33}SO_3^-K^+$	0.033	60	—	233(1)	—	Rosen, 1969
$C_{18}H_{37}OSO_3^-Na^+$	0.25	60	227	227(5)	151[b]	Weil, 1954
Sodium oleyl sulfate	0.25	60	246	240(5)	226[b]	Weil, 1954
Sodium elaidyl sulfate	0.25	60	243	241(5)	202[b]	Weil, 1954
$C_{12}H_{25}OCH_2CH(CH_3)OSO_3^-Na^+$	0.25	60	200	—	—	Weil, 1966
$C_{14}H_{29}OCH_2CH(CH_3)OSO_3^-Na^+$	0.25	60	215	—	—	Weil, 1966
$C_{14}H_{29}[OCH_2CH(CH_3)]_2OSO_3^-Na^+$	0.25	60	210	—	—	Weil, 1966
$C_{16}H_{33}OCH_2CH(CH_3)OSO_3^-Na^+$	0.25	60	200	—	—	Weil, 1966
$C_{18}H_{37}OCH_2CH(CH_3)OSO_3^-Na^+$	0.25	60	160	—	—	Weil, 1966
$C_{18}H_{37}OCH_2CH_2OSO_3^-Na^+$	0.25	60	160	—	—	Weil, 1966
o-$C_8H_{17}C_6H_4SO_3^-Na^+$	0.15	60	148	—	—	Gray, 1965
p-$C_8H_{27}C_6H_4SO_3^-Na^+$	0.15	60	134	—	—	Gray, 1965
p-$C_8H_{17}C_6H_4SO_3^-Na^+$	0.25	60	150	—	—	Gray, 1955
o-$C_9H_{19}CH(CH_3)C_6H_4SO_3^-Na^+$	0.15	60	165	—	—	Gray, 1965
p-$C_9H_{19}CH(CH_3)C_6H_4SO_3^-Na^+$	0.15	60	162	—	—	Gray, 1965
o-$C_{12}H_{25}C_6H_4SO_3^-Na^+$	0.15	60	206	—	—	Gray, 1965
o-$C_{12}H_{25}C_6H_4SO_3^-Na^+$	0.25	60	208	—	—	Gray, 1955
p-$C_{12}H_{25}C_6H_4SO_3^-Na^+$	0.15	60	201	—	—	Gray, 1965
$C_{10}H_{21}CH(CH_3)C_6H_4SO_3^-Na^+$	0.25	60	—	—	245	Smith, 1966
o-$C_{11}H_{23}CH(CH_3)C_6H_4SO_3^-Na^+$	0.15	60	190			Gray, 1965
p-$C_{11}H_{23}CH(CH_3)C_6H_4SO_3^-Na^+$	0.15	60	210	—	—	Gray, 1965
p-$C_{11}H_{23}CH(CH_3)C_6H_4SO_3^-Na^+$	0.25	60	218	—	—	Gray, 1955
p-$C_7H_{15}CH(C_4H_9)C_6H_4SO_3^-Na^+$	0.15	60	219	—	—	Gray, 1955
p-$C_7H_{15}CH(C_4H_9)C_6H_4SO_3^-Na^+$	0.25	60	230	—	—	Gray, 1955
$C_{12}H_{25}CH(CH_3)C_6H_4SO_3^-Na^+$	0.25	60	—	—	80	Smith, 1966
$C_{14}H_{29}CH(CH_3)C_6H_4SO_3^-Na^+$	0.25	60	—	—	10	Smith, 1966
o-$C_{15}H_{31}CH(CH_3)C_6H_4SO_3^-Na^+$	0.15	60	105	—	—	Gray, 1965
p-$C_{15}H_{31}CH(CH_3)C_6H_4SO_3^-Na^+$	0.15	60	129	—	—	Gray, 1965
$C_{16}H_{33}CH(CH_3)C_6H_4SO_3^-Na^+$	0.25	60	—	—	0	Smith, 1966
$CH_3CH(SO_3^-Na^+)COOC_{14}H_{29}$	0.25	60	220	—	240	Stirton, 1962
$C_2H_5CH(SO_3^-Na^+)COOC_{12}H_{25}$	0.25	60	200	—	225	Stirton, 1962
$C_7H_{15}CH(SO_3^-Na^+)COOC_8H_{17}$	0.25	60	—	—	185	Weil, 1960
$C_{10}H_{21}CH(SO_3^-Na^+)COOC_4H_9$	0.25	60	220	—	230	Stirton, 1962
$C_{10}H_{21}CH(SO_3^-Na^+)COOC_5H_{11}$	0.25	60	220	—	235	Stirton, 1962
$C_{14}H_{29}CH(SO_3^-Na^+)COOCH_3$	0.25	60	210	200(5)	225	Stirton, 1962
$C_{14}H_{29}CH(SO_3^-Na^+)COO^-Na^+$	0.25	60	175	165(5)	125	Micich, 1966
$C_{14}H_{29}CH(SO_3^-Na^+)COOC_2H_5$	0.25	60	210	—	215	Stirton, 1962
$C_{13}H_{27}C(CH_3)(SO_3^-Na^+)COOCH_3$	0.25	60	180	160(5)	200	Micich, 1966
$C_{16}H_{33}C(CH_3)(SO_3^-Na^+)COOCH_3$	0.25	60	175	165(5)	35	Micich, 1966
$C_{18}H_{37}C(CH_3)(SO_3^-Na^+)COOCH_3$	0.25	60	140	130(5)	30	Micich, 1966
$C_8H_{17}C(C_8H_{17})(SO_3^-Na^+)COOCH_3$	0.25	60	210	200(5)	215	Micich, 1966
$C_8H_{17}C(C_8H_{17})(SO_3^-Na^+)COO^-Na^+$	0.25	60	0	0	95	Micich, 1966
$C_8H_{17}C(C_6H_{13})(SO_3^-Na^+)COOCH_3$	0.25	60	204	190(5)	213	Micich, 1966
$C_8H_{17}C(C_4H_9)(SO_3^-Na^+)COOCH_3$	0.25	60	170	5(5)	200	Micich, 1966

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Table 7–2. (Continued)

Surfactant	Conc. (%)	Temp. (°C)	Foam Height (mm) Distilled Water Initial	Foam Height (mm) Distilled Water After Time (min)	Foam Height (mm) 300 ppm $CaCO_3$ Initial	Reference
$C_{12}H_{25}O(C_2H_4O)_{15}H$	0.25	60	—	—	197	Wrigley, 1957
$C_{12}H_{25}O(C_2H_4O)_{20}H$	0.25	60	—	—	195	Wrigley, 1957
$C_{12}H_{25}O(C_2H_4O)_{33}H$	0.25	60	—	—	180	Wrigley, 1957
$C_{16}H_{33}O(C_2H_4O)_{15}H$	0.25	60	—	—	153	Wrigley, 1957
$C_{16}H_{33}O(C_2H_4O)_{20}H$	0.25	60	—	—	167	Wrigley, 1957
$C_{16}H_{33}O(C_2H_4O)_{30}H$	0.25	60	—	—	149	Wrigley, 1957
$C_{18}H_{37}O(C_2H_4O)_{15}H$	0.25	60	—	—	165	Wrigley, 1957
$C_{18}H_{37}O(C_2H_4O)_{21}H$	0.25	60	—	—	152	Wrigley, 1957
$C_{18}H_{37}O(C_2H_4O)_{30}H$	0.25	60	—	—	115	Wrigley, 1957
$C_{18}H_{35}O(C_2H_4O)_{15}H^c$	0.25	60	—	—	140	Wrigley, 1957
$C_{18}H_{35}O(C_2H_4O)_{20}H^c$	0.25	60	—	—	160	Wrigley, 1957
$C_{18}H_{35}O(C_2H_4O)_{31}H^c$	0.25	60	—	—	140	Wrigley, 1957
t-$C_9H_{19}C_6H_4O(C_2H_4O)_8H$	0.10	25	55	45(5)	—	GAF, 1965
t-$C_9H_{19}C_6H_4O(C_2H_4O)_9H$	0.10	25	80	60(5)	—	GAF, 1965
t-$C_9H_{19}C_6H_4O(C_2H_4O_{10-11}H$	0.10	25	110	80(5)	—	GAF, 1965
t-$C_9H_{19}C_6H_4O(C_2H_3O)_{13}H$	0.10	25	130	110(5)	—	GAF, 1965
t-$C_9H_{19}C_6H_4O(C_1H_4O)_{20}H$	0.10	25	120	110(5)	—	GAF, 1965
t-$C_{23}H_{25}S(C_2H_4O)_{9-10}H$	0.30	43	215	35(10)	220^d	Pennsalt, 1956

[a] J. Ross and G. D. Miles, Am. Soc. Testing Materials, Method D1173–53, Philadelphia, Pa., 1953; *Oil and Soap* 18, 99 (1941).
[b] 0.11 in 100 ppm $CaCO_3$.
[c] From oleyl alcohol.
[d] 150 ppm hard water.

intermolecular cohesive forces in the adsorbed film as the oxyethylene content increases. Van der Waals forces between surfactant molecules decrease with increasing oxyethylene content, since the area per molecule at the surface increases with this change. However, the polyoxyethylene chain is believed to be coiled in the aqueous phase and the cohesive forces due to intra- and intermolecular hydrogen bonding are stated to pass through a maximum with increasing oxyethylene content. The summation of the van der Waals and hydrogen bonding cohesive forces consequently passes through a maximum as the oxyethylene content of the molecule is increased. In 300 ppm $CaCO_3$ solution at 60°C, polyoxyethylenated alcohols appear to be considerably better foaming agents than polyoxyethylenated fatty acids. Immediate foam heights for polyoxyethylenated *n*-dodecanol are higher than those for corresponding hexadecanol, octadecanol, or oleyl alcohol derivatives. Optimum oxyethylene content in these cases is at 15–20 moles of ethylene oxide per mole of hydrophobe (Wrigley, 1957). In distilled water at 25°C the optimum oxyethylene content for nonylphenol derivates is about 13 moles of ethylene oxide per mole of hydrophobe (GAF, 1965). Homogeneous (single specie) polyoxyethylenated materials show higher initial foam heights but lower foam stabilities than commercial materials of the same nominal structure (Crook, 1964).

The foam of polyoxyethylenated nonionics decreases markedly at or above their cloud points. This has been atributed to a rate effect, the cloud point being marked by the aggregation of the dehydrated micelles into larger aggregates. Diffusion of surfactant molecules from these aggregated micelles to the newly created interface involved in bubble formation might be much slower than from the smaller, more highly hydrated micelles, thus decreasing the stabilization of the liquid lamellae in the forming foam (Dupre, 1960).

Low-foaming surfactants of the polyoxyethylenated nonionic type have been produced by adding a second hydrophobic group to the molecule at the end away from the first hydrophobic group. Measurements of the surface area per molecule in these products indicate a much more expanded, less coherent surface film as a result of this modification of structure. The low-foaming properties are believed to be due, at least in part, to this low coherent surface film (Dupre, 1960). Foams with very poor stability are also obtained with surfactants of the type $RCH[O(CH_2CH_2O)_mH]_2$ containing two polyoxyethylene chains. Although initial foam heights in some cases approximate those of conventional polyoxyethylenated nonionics of the type $RO(CH_2CH_2O)_xH$, the foam produced by the acetal type

surfactants decreases to a very small volume in a few minutes (Kuwamura, 1972). Placing methyl groups at the ends of the polyoxyethylene chains away from the hydrophobic group, in these cases, too, produces even lower foam volumes and foam stabilities, together with larger surface areas per molecule (Takahashi, 1973).

IV. FOAM-STABILIZING ORGANIC ADDITIVES

The foaming properties of surfactant solutions can be modifed greatly by the presence or addition of other organic materials. Solutions that show excellent foaming properties can be converted to low- or nonfoaming materials and those that show poor foaming properties can be converted to high-foaming products by the addition of small amounts of the proper additive. Because of its practical importance, this method of modifying foaming properties has been extensively used and investigated.

Additives that increase the rate of attainment of surface tension equilibrium act as foam inhibitors by decreasing film elasticity while those that decrease the rate of attainment of that equilibrium act as foam stabilizers. Additives that decrease the rate of attainment of surface tension equilibrium may do so by decreasing the critical micelle concentration of the surfactant solution, thereby lowering the activity of the monomeric surfactant in solution and its rate of migration to the surface. On the other hand, additives that cause the breakdown of micelles, with the consequent increase in the activity of the monomeric surfactant, increase the rate of attainment of surface tension equilibrium and decrease foaming (Ross, 1958). Another mechanism by means of which additives can act as foam stabilizers is by increasing the mechanical strength of foam films. The surface films produced by solutions of highly purified surfactants are often weakly coherent films, containing molecules that are relatively widely spaced because of the mutual repulsion of the oriented polar heads. These films are mechanically weak and nonviscous. When they constitute the interfacial film in the lamellae of a foam, liquid drains rapidly from the lamellae. The addition of the proper additive to this type of film can convert it to a closer-packed, more coherent one of high surface viscosity, which is slow-draining and produces a much more stable foam.

The most effective additives for increasing the stability of the foam produced by surfactant solutions appear to be long-chain, often water-insoluble, polar compounds with straight-chain hydrocarbon groups of approximately the same length as the hydrophobic group